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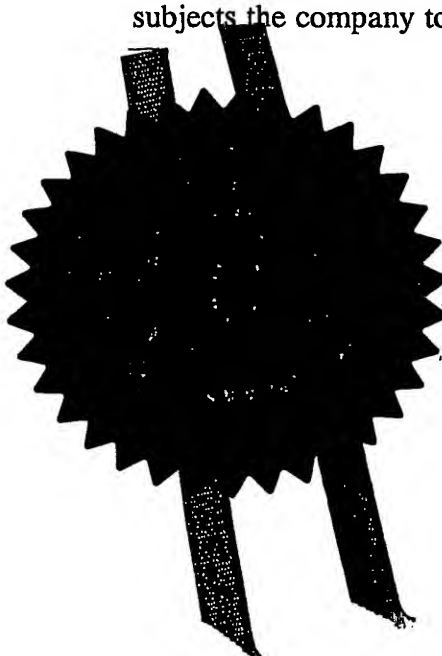
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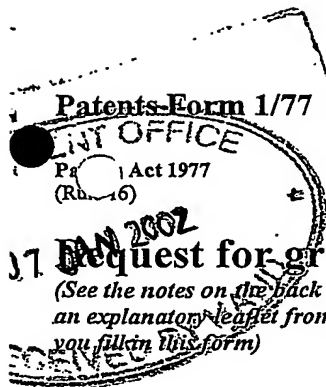
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2. Patent application number **0200260.8**
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If the applicant is a corporate body, give the country/state of its incorporation **UK**

4. Title of the invention **MICROPARTICLES AND METHODS OF MAKING THEM**

5. Name of your agent (if you have one) **MEWBURN ELLIS**
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MICROPARTICLES AND METHODS OF MAKING THEM

The present invention relates to microparticles and
5 in particular to those in the nanoparticle range, and to
such particles which are used in catalysis, as well as
methods of making them.

It has been known to be desirable for some time
that solid microparticles having catalytic activity
10 should be preferred for liquid phase catalysis, because
on the one hand macro catalysts have clear disadvantages
from the point of view of atom efficiency, while soluble
catalysts, although theoretically efficient, present
great difficulties of separation.

15 However, the desire for the microparticles to be as
small as possible so as to achieve the greatest possible
efficiency conflicts in principle with the ease of
separating them from the liquid reaction medium if, for
example, filtration or like methods of separation are
20 attempted.

It is for this reason that there has been interest
in magnetically susceptible catalytic microparticles
which are dispersible in the liquid reaction medium but
which are able to be coagulated under the influence of a

magnetic field and thereby readily separated from the medium. They can then be re-dispersed for re-use.

However, the problem then arises that many ferromagnetic materials would react with the reaction mixture; it is therefore necessary to protect the ferromagnetic particles by a coating of some material which is inert to the medium.

In JP-A-02069904, for example, there is disclosed a way of "rust-proofing" a magnetic metal powder by contacting the preformed powder with carbon monoxide, methane or ethane and hydrogen at high temperatures. It is stated that the saturation magnetizations of the magnetic metal films (sic) obtained is not lowered substantially.

Another method which has been used is that of an arc discharge. In IEEE Transactions on Magnetism, 32, No. 5 of September 1996 at page 4511-4513, Jeyadevan et al, after reviewing earlier attempts at encapsulation using arc discharges proposed to coat pre-existing magnetic particles with a surfactant and then treat them in an arc so that the surfactant is reduced or decomposed to a carbon that encapsulates the magnetic particles. The size of the magnetic particles was

stated to be an average diameter of 10 nm and the surfactant used was sodium oleate.

5 Turgut et al J. Appl. Phys. 81 (8) of April 1997 at pages 4039-4041 disclose another arc discharge process and state that in this case many of the particles were only nominally coated or uncoated. The interest in that disclosure concerned the crystalline structure of the magnetic nanocrystals. All of these processes have extremely low yields.

10 Yet another approach is seen in WO-A-99/46782 of Universiteit Utrecht. The inventor is Geus, and this document will be preferred to as "Geus" hereafter.

15 This takes an approach different from that of the rest of the prior art. Ferromagnetic material is deposited on the surface of an alumina support. A graphite coating is then applied and the alumina support is dissolved away leaving particles which are allegedly entirely coated with graphite. The Geus disclosure will be discussed in more detail later.

20 However, it is clear from the above that all prior processes have been ones which require complex preparative stages before the coated ferromagnetic microparticles were achieved.

In contrast, we propose a direct method for the formation of ferromagnetically nucleated graphite-protected microparticles. Furthermore, we find that using this method provides particles within a close size
5 range and with little or no loss in magnetic susceptibility as compared to the pure magnetic material.

After the microparticles have been prepared, catalytically active components such as palladium
10 metallic clusters can be supported on the external surface.

This results in a highly active carbon-supported catalyst for chemical reactions, especially hydrogenation reactions, in the liquid phase.

15 The chemically and mechanically robust microparticles (usually in the nanoparticle size range) are shown to disperse well in aqueous or organic solvent and form a stable dispersion and exhibit an excellent and consistent mass transfer so as to sustain a high
20 catalytic rate of reaction.

We find that the coating has very high coherence so that the core is not exposed to the reagent, there is high yield and, as already mentioned, there is a high degree of uniformity of size.

The process involves the solidification of droplets of a solution containing soluble salt(s) or complex(es) of the ferromagnetic element(s) or alloy(s) and decomposable sources of carbon and of a heteroatom such as nitrogen, and pyrolysis of the solids to form a graphitic/hetero encapsulating shell around a ferromagnetic core. The source of carbon and of the heteroatom is preferably the salt or complex itself/themselves. For example cyanides, isocyanides, cyanates or isocyanates, especially as ligands, are decomposable in the pyrolysis to yield a graphitic shell including nitrogen atoms.

Other heteroatoms which may be used are, for example, B, P, or O. Solidification may be the first phase of pyrolysis; or it may be a precipitation occurring as a result of contact with a precipitant such as, for example, ammonia.

The solution may further contain a source forming an amorphous matrix on pyrolysis. Decomposable such sources include polyvinyl alcohol (PVA), preferably partially hydrolysed, polyvinyl pyrrolidone (PVP) or other polymers. Inorganic sources, especially of calcium, may contribute.

The sources may act to dilute the ferromagnetic and graphitic source species to prevent wasteful agglomeration of microparticles via their graphitic layers.

5 However the amorphous mass may contain individual microparticles.

To prepare catalytically-active particles, the carbon surface whether of the microparticles or of a matrix contacting them may be functionalized e.g. by
10 acid treatment, for carrying catalytic functions such as metals. These catalytic functions may be added by conventional procedures.

Particular solution systems may be as follows:

Nickel-iron alloy microparticles can be prepared
15 from iron nitroferricyanide $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$ -nickel nitrate solution. Other systems include Fe/Ca; Fe/Zn, Fe/Cu, Fe/Mn, Fe/Co, Fe/Ni, Fe/Mg, Fe/Pt composites, or their carbides, oxycarbides, oxides and mixed oxides as inner cores within the encapsulation.

20 Typically, other carbon-coated Fe based alloys or mixed composites cores can be prepared via an aqueous solution of iron cyanide containing precursor, $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ mixed with aqueous solutions of $(\text{CH}_3\text{COO})_2\text{Co} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$,

$(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{PtCl}_4(\text{NH}_4)_2$
(in a 1:1 Fe:M molar ratio), respectively.

In many of these systems there is variability in the metal/carbon atomic content of the salt or complex.
5 Adjustment of this ratio affords a means of adjusting the average thickness (number of layers) of encapsulation graphite.

We provide also microparticles which are characterized by the presence of hetero-atoms (usually
10 nitrogen, but possibly B, P, O, etc., and probably about 2-7 atom %) in an otherwise graphitic carbon shell surrounding and encapsulating a ferromagnetic core. These hetero elements provide curvature of a fullerene type so that a more complete enclosure of the core is
15 achieved without the faults or fractures of a purely graphitic structure. Furthermore, the microparticles will preferably have a calculated average diameter of the order of 10-15 nm.

The more complete covering afforded by the carbon
20 shell and the regularity of size of the particles are great advantages in the context of liquid-phase catalysed reaction.

With such small magnetic catalyst bodies, the advantages of homogeneous (or colloidal) and

heterogeneous catalysis may be combined since, while there is no agglomeration, the catalytic sites per area on the small particle are optimised and very well accessible. Application of external magnetic field leading to agglomeration of these magnetic particles facilitates their separation from product. Apart from catalysis application, other useful applications of such carbon-encapsulated nanometer sized particles may also be expected in several fields of technology.

10 In the accompanying drawings:

Figure 1 is a schematic diagram of a nano-size soft magnetic alloy encapsulated in quasi-spherical graphitic shells;

15 Figures 2a and 2b (comparative) are X-ray diffraction patterns for Geus particles before and after acid treatment, respectively;

Figures 3 and 4 (comparative) are respectively high (x 800,000) and low (x 46,000) Transmission electron microscope (TEM) micrographs of Geus particles;

20 Figure 5 is an X-ray diffraction pattern (XRD) of the present particles after acid treatments;

Figure 6 is a low-resolution TEM micrograph of a present sample before pyrolysis;

Figure 7 is a high resolution TEM micrograph of present particles after pyrolysis;

Figure 8a is an X-ray photo-electron spectroscopic (XPS) record demonstrating the presence of heteroatoms
5 in the shell;

Figure 8b is an XPS spectrum of the N region of the particles before heating;

Figure 9 is a vibrating sample magnetometer (VSM) graph of a present sample before acid functionalization;

10 Figure 10 is a graph showing the catalytic activity of a present catalytic sample;

Figure 11 is an XRD spectrum of a second embodiment of particle after pyrolysis;

Figures 12 and 13 are a low resolute TEM micrograph
15 of the second embodiment before and after pyrolysis respectively;

Figure 14 is a high resolution TEM micrograph of the second embodiment after pyrolysis;

Figures 15 and 16 are VSM and EDX records
20 respectively of the second embodiment after pyrolysis; and

Figures 17 and 18 are high- and low-resolution TEM micrographs respectively of particles of a third embodiment.

System Example 1 (comparative)

Preparation of carbon encapsulated nickel-iron nanoparticles on a solid support (alumina) via gaseous methane decomposition (Geus method)

5 We adopted and modified the method of Geus. Alumina-supported nickel-iron alloy particles were prepared by a general controlled deposition-precipitation method as follows: a solution containing nickel compound was prepared by dissolving 2.0 g of
10 nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into 10.0 ml of (DI) water. 4g of activated alumina were added to the solution and the pH was adjusted to 5. An aqueous solution containing iron compound (2g of sodium nitroferricyanide (III) dihydrate $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}]$ in
15 10.0 ml. DI water was then added to the mixture at a rate of 1 ml/min under vigorous stirring giving in total 1:1 molar ratio of Ni:Fe. The solid material was filtered, extensively washed, dried overnight at 120°C and calcined at 300°C in a flowing stream of 30 ml/min
20 air for 3h. formation of alloy particles on alumina was conducted by controlled reduction of the solid at 700°C (with a temperature programmed ramping from room temperature to 700°C at 6°C/min) under a flow rate of 100 ml/min 20% H_2 in nitrogen for 2h. Deposition of

carbon was then carried out by placing the solid at 700° in a stream of 20% methane in nitrogen at a total flow rate of 100 ml/min. After completing the carbon encapsulation the resulting solid was cooled to room temperature in a flow of nitrogen. The alumina support was allowed to dissolve in boiling concentrated HCl at 120°C for 15h. The solid was collected, exhaustively washed and dried.

10 **Synthesis Example 2**

Preparation of carbon encapsulated nickel-iron nanoparticles directly from solution (inventive method)

Three aqueous solutions (2g of nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 10.0 ml of DI water; 1 g of polyvinyl alcohol of MW 31,000 to 50,000 in 100 ml DI water; 2g of sodium nitroferricyanide (III) dihydrate [$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$] in 10.0 ml DI water) were mixed together. The solution mixture was allowed to pass to the pneumatic sprayer head kept at 20 psi N_2 gas. the fine mists containing these solution mixture were sprayed into the headspace of a jar filled with 0.88 sg saturated ammonia solution. In the case of ammonia treatment the fine droplets will immediately form solid precipitates when in contact with ammonia (vapour and

solution). The solid was then collected, extensively washed, dried and calcined at 900°C for 10h.

Synthesis Example 3

5 Preparation of carbon encapsulated nickel-iron nanoparticles directly from solution (inventive method)

The fine mists generated as in Synthesis Example 2 but from a solution lacking PVA were sprayed directly into a hot zone of a furnace at 900°C with a counter
10 current of N₂ at 15 ml/min. As they enter the zone the droplets solidify but then fuse and calcine as before to yield nanoparticles encapsulated by graphitic/heteroatom layers as before.

15 Synthesis Example 4 Fe/Ca system leads to carbon-encapsulated Fe₃C nanoparticles (inventive method)

The same iron source, Na₂Fe(CN)₅NO.2H₂O, is used as in the previous examples. An aqueous solution of this
20 iron precursor is mixed with an aqueous solution of Ca(NO₃)₂.4H₂O in a 1:1 Fe:Ca molar ratio and followed by the Spray Precipitation protocol (Example 2).

The Fe/Ca system enables the obtaining of a very high concentration of carbon-encapsulated nanoparticles

with a very narrow size distribution. The XRD spectrum (Figure 11) shows that this sample consists of Fe_3C nanoparticles encapsulated in concentric graphitic carbon layers with $\text{Ca}(\text{OH})_2$, CaCO_3 and related Ca-containing species. EDX indicates the presence of Ca and iron rich material (Figure 16). TEM micrographs of the sample after calcination show that the iron carbide nanoparticles are encapsulated in graphitic carbon (Figures 12-14), the amorphous calcium-containing phases forming matrices between the graphitic-coated iron carbide particles (Figure 13). We attribute this to the fact that calcium would not form a stable alloy with iron (vs Fe-Ni) but its presence with the Fe-based nanoparticles (Figure 14) protects the composite material from sintering during the heat treatment in N_2 , hence providing a very high concentration of carbon coated iron containing nanoparticles with a very homogeneous size. Microanalysis of the product shows that it contains Ca- 35.49wt% and Fe- 29.57wt%. Adding excess acidified water to the final material allows removal of particularly the calcium-containing matrix (63.3mg Ca and 37.06 mg Fe could be leached out from 200 mg solid in the 50mL HCl solution), releasing the tiny colloidal graphitic carbon-encapsulated magnetic Fe_3C

nanoparticles. These carbon coated particles contain Ca 3.6wt% and 10.89wt% Fe.

Iron carbides Fe_2C , $\text{Fe}_{2.2}\text{C}$, Fe_5C_2 and Fe_3C all are ferromagnetic, displaying a high coercive force. Fe_3C is known to give a high magnetic response but its extreme air sensitivity limits its uses. It is exciting that this technique can prepare macroscopic quantity of magnetic carbon-encapsulated iron carbide nanoparticles. Figure 15 shows that our sample displays a saturation magnetization of 90 emu/g. It is apparent that this material is quite air-stable; presumably the graphite coating offers protection against oxidation.

TEM imaging (Figures 17,18) clearly shows graphitic encapsulation of other systems such as Fe/Mn indicating the generic nature of the method.

Synthesis Example 5

Noble metal deposition onto the carbon nano-materials

The catalyst component (heterogeneous catalyst or homogeneous catalyst species) may be directly deposited onto the external surface of the carbon coated nano-magnet composites. However, it is desirable to functionalise the external carbon surface. Accordingly, the surface of the carbon encapsulated alloy particles

prepared by the method of Example 1 on the one hand or Examples 2 or 3 on the other was functionalised with -OH or -COOH groups by immersing them into boiling concentrated HCl (acid treatment) or diluted bleach (NaOCl with and without H₂O₂) solution. For some applications an acid or bleach washing step is advantageous to remove traces of uncoated metal or metal oxide. The surface activated carbon particles were then collected, washed and dried. A wetness impregnation method was then applied in order to deposit 5% Pd onto these carbon based materials (an appropriate amount of Pd (II) acetylacetonate was allowed to dissolve in acetone/water mixture at pH=10 and then stirred with the solid for 3 h at room temperature; the solid was then collected after extensive wash with acetone and air drying at room temperature).

Example 6: Catalyst testing

6.5 ml of nitrobenzene was dissolved into 125.0 ml of isopropanol (IPA) as a solvent (well dispersed) and was placed in a glass beaker inside the 30 ml batch stainless steel Parr reactor. 30 mg of the carbon-based catalyst was then added. The reactor was purged with a nitrogen flow for 5 minutes followed by intermittent

purges with pure H₂ at 2000 kPa (20 bar). This ensured that the reactor was actually filled with pure H₂ without trapping any other gases. The reactor was kept at 2000 kPa (20 bar) and heated up to 80°C with a constant
5 stirring. Samples (<1 ml) were collected at different times from the reactor via the internal sampling dip tube without seriously disturbing the on-going reactions. The samples were analyzed by HPLC. For the hydrogenation of nitrobenzene, aniline was the major
10 product observed.

Example 7: Material characterization

In order to determine the formation of Fe-Ni alloy and graphitic carbon structure X-ray powder diffraction
15 (XRD) was carried out. XRD patterns were recorded at room temperature using the Cu K α radiation ($\lambda = 1.54056 \times 10^{-8}\text{m}$).

The materials were also examined using a Philip CM20 high-resolution transmission electron microscope
20 (TEM) operating at accelerating voltage of 200kV. Samples were suspended in isopropanol. A few drops of the suspended solution were put onto a copper grid covered with a holed lacey carbon film prior examination.

Magnetic measurements were performed using a vibrating sample magnetometer (VSM), which consisted of an electromagnet (maximum applied field of $\pm 1200 \text{ kAm}^{-1}$) with a sample cell holder vibrating between two pole
5 faces. Powder samples were prepared by placing a small amount of wax in the base of a brass sample holder, followed by topping it with approximately 50 mg of the powder sample. The powder was set in place by dripping a small amount of molten wax on top and then plugging
10 with a brass stopper, which was then put into a Perspex outer sheath. The sample was then aligned by placing the holder in boiling water to melt the wax and cooled in an applied field of 2T. The sample was then magnetised to saturation in a pulsed magnetic field (up
15 to 9T) parallel to the direction of measurement. The sample was held at the end of a rod linked to an oscillator, causing the sample to vibrate in a direction perpendicular to the applied field between detection coils positioned on the pole tips of an electromagnet.
20 A current was passed through the coils of the electromagnet producing an applied field that was measured using a Hall probe. Various fields were applied allowing time for the field to stabilise each time, thus eliminating any signals being produced in the

coils due to the applied field. the vibration of the sample generated an AC signal from the coils proportional to the magnetisation of the sample. A frequency of 70-80Hz was used, as there was a minimum of background noise in this range. Hence, the VSM measured the difference in magnetic induction between a region of free space with and without the sample as it vibrated giving a direct measure of the magnetisation M . While the sample is in the magnetic field the magnetic induction was $B_M = \mu_0(H+M)$ as the sample was moved away this changes to $B_0 = \mu_0 H$ this gave the change in magnetic induction $\Delta B = \mu_0 M$, B - magnetic induction, H - magnetic field, M - magnetisation, μ_0 - permeability of free space.

Temperature programmed oxidation was carried out using a home-built apparatus. Carbon sample (50 mg) was sandwiched between two silica wool plugs in a quartz reactor tube housed in a temperature controlled tubular furnace. Diluted air (5% O_2) was allowed to flow through the sample at a constant flow rate (2 ml/min). A quadruple mass spectrometer was used to monitor the exit gas (mass fragments) continuously without much delay since the dead volume between the mass spectrometer and the reactor tube was carefully minimised. The sample

was ramped at 10°C/min from 150-400°C and then 2°C/min from 400-900°C under the same flow rate. Since different forms of carbons (amorphous, tubular, graphitic, enclosed) react with oxygen at different temperatures (different in chemical reactivity) hence with calibration their differentiation is achieved.

Results of Material Characterization

A: Geus method - Synthesis Example 1

10 XRD measurement (Figure 1a) on the calcined alumina-supported cyanide precursors after H₂ reduction and methane treatment as according to Geus show clearly the characteristic peaks of graphitic structure ($2\theta = 26.63^\circ$, $d = 3.345$), FeNi (1:1) alloy ($2\theta = 43.73^\circ$ and 50.93° with $d = 2.069$ and 1.792 , respectively) and alumina ($2\theta = 67.33^\circ$). No peak is matched to individual metal (for Fe, $d = 2.027$ and 1.433 ; for Ni, $d = 2.034$ and 1.762) or metal oxide peaks (for Fe₂O₃, $d = 2.518$ and 2.953 ; for NiO, $d = 2.088$, 2.412 , 1.477 and 1.476 ; for (Ni, Fe) Fe₂O₄, $d = 2.520$, 1.479 , 1.610 , 2.950 and 2.091) suggesting alloy (FeNi with $d = 2.080$ and 1.800) is favourably formed on the porous alumina support. The calculated average particle size of the alloy after accounting for the instrumental peak broadening is about

36.6 nm. Acid treatment of this material leads to retention of 6.1% wt of acid insoluble material (Geus/methane/850°C).

5 The XRD measurement (Figure 1b) clearly indicates that the alumina support is removed (peak at $2\theta = 67.33^\circ$ removed) by the acid treatment; however, it also appears to dramatically reduce the alloy intensity relevant to graphitic structure and shifts the average alloy particle size to 16.7 nm.

10 TEM clearly shows that some alloy particles are encapsulated in polygonal graphitic structures (Figures 3 and 4); however, their size distribution is extremely broad (10 to 200 nm). Energy Dispersive X-Ray (EDX) analysis confirmed the presence of Fe and Ni. The
15 numbers of the encapsulated graphitic layer vary from particle to particle and more than 15 layers of carbons are commonly found. Also, there are many other forms of carbon structures (amorphous, graphitic, tubular, whisker, fibres, onions, encapsulated carbons, etc.)
20 observed. After the acid treatment the alumina support and incomplete carbon coated metal/metal oxide are removed. The final product contains mainly carbon structures (tube, amorphous, fibres, onions, etc.) the principal form of which is found to be the tubular

carbon. It is noted that there is very small amounts of carbons still containing metallic inner cores present in the final product.

B: Product of method embodying the invention -

5 **Synthesis Example 2**

XRD measurement clearly indicates the presence of alloy peaks ($2\theta = 43^\circ$ and 51° with $d = 2.07$ and 1.79 , respectively) in a correct intensity ratio. The calculated average particle size is considerably smaller than the material prepared by the Geus method. In order to provide a carbon support to each of these coated alloy nanoparticles soluble polyvinyl alcohol (PVA hydrolysed, MW 31,000 to 50,000) is added to the solution prior to spraying. Polyvinyl alcohol is known to decompose readily at elevated temperatures (ca 120°C) hence it is a carbon source for an amorphous matrix. XRD in Figure 5 shows that the calculated average encapsulated core size is 11.0 nm with the three distinctive Fe:Ni alloy peaks. There is only a very small broad hump near the 2θ of 26° indicating consistently only a few atomic layers (even after pyrolysis of the composite material at 900°C). 35% wt of insoluble material is retained under identical acid

10

15

20

treatment conditions as were employed for the Geus samples.

Figure 6 shows a typical low-resolution TEM micrograph of the present precipitation sample. It is
5 interesting to see many nanoscopic size particles with a very uniform particle size distribution. The particle contains Fe and Ni as confirmed by the EDX analysis. Direct measurement on the micrograph shows that a majority of the encapsulated particles are in the size
10 range of 10-15 nm.

High resolution TEM micrographs (Figure 7) indicate that all the particles are found exclusively encapsulated in the quasi-spherical graphitic structures. These graphitic encapsulated particles are
15 embedded in amorphous carbon material (the relative amount depends on the amount of polyvinyl alcohol used). Detailed examination of the quasi-spherical carbon coatings show that in many cases, carbon lattice fringes (ca. $3.4 \times 10^{-8}\text{m}$) could be traced, yielding surprisingly
20 concentric carbon shelled structures. Only short exposure of the selected area to the electron beam is ensured (<60 s) hence there is no possibility of carbon shelled structure formation being due to the electron beam illumination. Attempts to obtain a lattice image

of the core particle were not successful on a Philips CM20 TEM microscope. It is believed that the fringe separations of the alloy particle ($2.09 \times 10^{-8}\text{m}$, $1.79 \times 10^{-8}\text{m}$) are beyond the resolution of the microscope used
5 ($>2.4 \times 10^{-8}\text{m}$).

Figure 8a shows XPS survey spectra of carbon-coated FeNi nanoparticles after encapsulation at 900°C but before acid treatment to remove any non-fully encapsulated particles. An XPS survey was recorded on
10 the sample without pre-treatment (before heating) and after it has been heated *in situ* at 250°C for 30 minutes to desorb some possible contaminants. No major changes are observed in the resulting data. The spectra are very similar - upper line being before treatment and
15 lower line after - showing the reproducibility of this measurement. All binding energies are given with an uncertainty of 0.2 eV on the absolute value. No charge effect being observed, the peaks are directly referenced to the carbon C1s peak at 284.6 eV.

20 It appears that the surface (or the first few atomic layers) contains essentially carbon but also with a small amount of other hetero-atoms (O, N, Na, Fe, Ni, etc). We detected small signals of Fe and Ni 2p and Auger peaks with the C:Fe and C:Ni atomic ratios being

at around 0.05. This fact agrees with the TEM images in showing that the Fe/Ni are species totally encapsulated by carbon cages after heat treatment in N_2 at $900^\circ C$ because their signals are not strong. The binding energies of these exposed Fe and Ni species suggest that they are unlikely to be in metallic states. An oxygen signal is also found. It is not yet clear whether O is attached to the exposed iron/nickel species, or to nitrogen or carbon. Also, there are traces of sodium (Nals peak) in the calcined sample which probably came from the iron precursor used.

It is interesting to find that a nitrogen signal is observed. The surface contains nitrogen in an atomic ratio of 43:3 C to N. the N1s region (Figure 8b) consists in a main peak at 398.6 eV with a shoulder at 400.8 eV. It is not yet sure when the nitrogen is located. It has been reported that a N1s signal at 401 eV is characteristic of nitrogen atoms present in graphene sheets it is thus concluded that a small amount of nitrogen is incorporated into the graphene network. It has also been reported that a strong peak at 398 eV with a shoulder at 400 eV was attributed to different C-N bonding (C=N and C-N). Hence we suggest that the carbon coating formed around the alloy particles during

the heat treatment at 900°C has a graphitic-like structure containing some nitrogen atoms. Nitrogen incorporation into graphene layer is probably responsible for the curvature of the graphitic planes resulting in encapsulation. The carbon coating of the nanoparticles prepared according to the Precipitation method contains 7 surface atom % of nitrogen that may make these encapsulated particles fundamentally and structurally different from the ones produced by the Geus method whose carbon jacket contains only carbon atoms and hence is made up of essentially planar plates.

Magnetic properties

Figure 9 shows the experimentally measured saturation magnetization of a typical spray-precipitation-pyrolysis sample. The material exhibits a saturation magnetization of 110 emu per gram mass of the sample at >1000 Oersted. We estimate from the TG experiments (not shown) that this typical carbon encapsulated nano-alloy sample contains 67% alloy content. Thus with taking account of the alloy content which mainly contributes to the magnetization (the graphite jacket is thought to contribute insignificantly as compared to the central soft magnetic Fe-Ni alloy

core) the saturation magnetization of this material per gram of alloy would be 165 emu/g. Literature value of bulk nickel-iron alloys of Ni:Fe ratio of 1.0 indicates 156 emu/g. Hence, within experimental error the present encapsulated alloy material appears to display a similar saturation magnetization as the bulk alloy. Table 1 summarises the comparison of the saturation magnetization values displayed by the spray-precipitation-pyrolysis sample with the literature values using the alumina-supported alloy particles with and without acid treatment.

Table 1. The normalised saturation magnetization values per gram of Fe-Ni alloy in the two samples

Sample	After encapsulation			After HCl treatment	
	Alloy content (wt%)	Ms (emu/g)	Hc (Oe)	Ms (emu/g)	Hc (Oe)
Spray-precipitation-pyrolysis	67%	165	1000	105 (8 hrs)	1000
Alumina-supported alloy	18.8%	130	100	48 (30 mins)	50

It is noted from the Table 1 that the slightly lower saturation magnetization of the Ni-Fe alloy on alumina (130 emu/g) reported by Geus could be due to an incomplete reduction of metal oxides to alloy. Because of the much higher alloy content in the spray-precipitation-pyrolysis sample than Geus sample it displays a higher saturation magnetization value per gram of sample mass (110 vs 24.4). It is interesting to find that the saturation magnetization decreases when samples are treated with acid (36% decrease in the spray sample vs 63% in the alumina sample). It is believed that the decrease in saturation magnetization has to be caused by dissolution of alloy particles, which have not been fully encapsulated by carbon layers. Hence, we believe that a larger quantity of fully encapsulated particles is made using the spray-precipitation pyrolysis technique whereby the impermeable graphitic

layers offer a total protection to the encapsulated nanoparticles against leaching in the strong acidic environment. On the other hand, Geus method does not provide a full protection of its encapsulated particles against acid treatment. Notice that the removal of alumina support would require acid treatment in order to release the carbon encapsulated Fe-Ni particles. It is however not entirely necessary for the spray samples where no support material is present. Even without acid treatment the present samples can equally disperse in aqueous medium very well as a colloid and without any significant attenuation in their saturation magnetization when the samples are pre-treated with a bleach solution (mild oxidation to introduce surface functionalities - such as phenolic and carboxylic groups on the carbon surface) at pH 9. These surface groups with different ϵ surface potentials provide anchoring points for catalyst (homogeneous or heterogeneous) immobilisation. At different pH, they also play a significant role for the particle dispersion or flocculation in the solvent.

Catalytic action

Figure 10 shows the 5% Pd impregnated spray-precipitation-pyrolysis sample is an active catalyst for the hydrogenation of nitrobenzene to aniline. Table 2 shows the comparison of the initial rate of reaction (extrapolation to time zero) of this material with a commercial Pd/C catalyst.

Table 2 showing the initial rates of nitrobenzene hydrogenation over two Pd samples

Catalyst	Initial rate (μ -mole of nitrobenzene converted to aniline s^{-1})
5% Pd/spray-precipitation-pyrolysis sample	1.529 (32 mg catalyst)
5% Pd/C (a commercial catalyst)	0.835 (50 mg catalyst)

10

It is found that the present catalyst shows almost double the rate of hydrogenation than a commercial catalyst with the same metal loading. We attribute the higher activity of the Pd doped spray sample in nitrobenzene hydrogenation to the better Pd dispersion onto the nano-size carbon particles (colloidally dispersed in the solvent) as compared to the micro-size commercial catalyst powder. The flocculation of the nano-size magnetic catalyst particles is easily achieved by applying an external magnetic field, which facilitates its filtration from the product solution.

15

20

In general, premature clustering of ferromagnetic particles can be prevented by using soft ferromagnetic materials in which the remanent magnetic moment (the magnetic moment in the absence of a magnetic field is low. The measured 110 emu per gram of the present (the saturation magnetization is greater than pure iron particles) allows effective precipitation (separation) or re-dispersion of the particles in liquid phase by simply switching the external magnetic field on or off.

10 The magnetic interaction between magnetic particles can be modulated by the application of 'spacer' materials between the magnetic particles such as the number of carbon shells and the background amorphous carbon. By changing the relative concentration of the metal
15 complexes and carbon sources (polymer + ligands) or changing the droplet size (using different spray heads) the overall magnetic properties of thee particles can be finely tuned.

Carbon encapsulation may be extended to other soft
20 magnetic materials such as Fe_3C , FeCu, Fe-Mn, Fe-Zn and Fe-Co using the present method.

CLAIMS

1. A method of forming microparticles with a ferromagnetic core encapsulated in a graphitic shell
5 containing hetero atoms which includes solidifying and pyrolysing droplets of a solution containing at least one source of a ferromagnetic metal, carbon and the hetero atoms.
2. A method according to claim 1, wherein the
10 microparticles are nanoparticles.
3. A method according to claim 1 or claim 2, wherein the solidification is carried out by precipitation of the droplets.
4. A method according to claim 1 or claim 2,
15 wherein the solidification is carried out by injection of the droplets into the pyrolysis zone.
5. A method according to any one of the preceding claims, wherein the hetero atoms are N, B, P or O.
6. A method according to claim 5, wherein the
20 hetero atoms include N and the source of the ferromagnetic metal is at least partly ferric cyanide, isocyanide, cyanate or isocyanate.

7. A method according to claim 6 wherein there is also present a source of Ni, Ca, Zu, Cu, Mn, Co, Mg or Pt as part of the ferromagnetic metal.

5 8. A method according to claim 7 wherein the solution includes iron nitroferricyanide and nickel nitrate.

9. A method according to any one of the preceding claims, wherein the solution additionally contains a diluent.

10 10. A method according to claim 5, wherein the diluent is a decomposable carbon-containing compound to form an amorphous matrix upon pyrolysis.

11. A method according to any one of the preceding claims including the step of treating the surface of the particles and/or the matrix to produce catalytic activity.

12. A method according to claim 11, wherein the treatment includes deposition of a catalytically active metal.

20 13. Microparticles having a ferromagnetic core encapsulated by a graphitic/hetero curved shell.

14. Microparticles according to claim 13, wherein the curved shell is of a plurality of onion-skin layers.

15. Microparticles according to claim 13 or claim 14 which are 10-15 nm diameter.

16. Microparticles according to claim 13, claim 14 or claim 15 which are embedded in an amorphous matrix.

5 17. Microparticles according to any one of claims 13 to 16 which have a catalytically-active surface.

18. Microparticles according to claim 16, wherein the matrix has a catalytically-active surface.

10 19. Microparticles according to claim 17 or claim 18, wherein the catalytic activity is due to a metal deposited on the surface.

20. Use of microparticles according to any one of claims 17 to 19 as catalyst in a liquid-phase reaction.

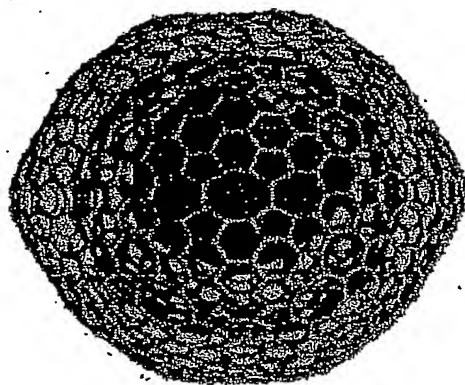


FIG. 1

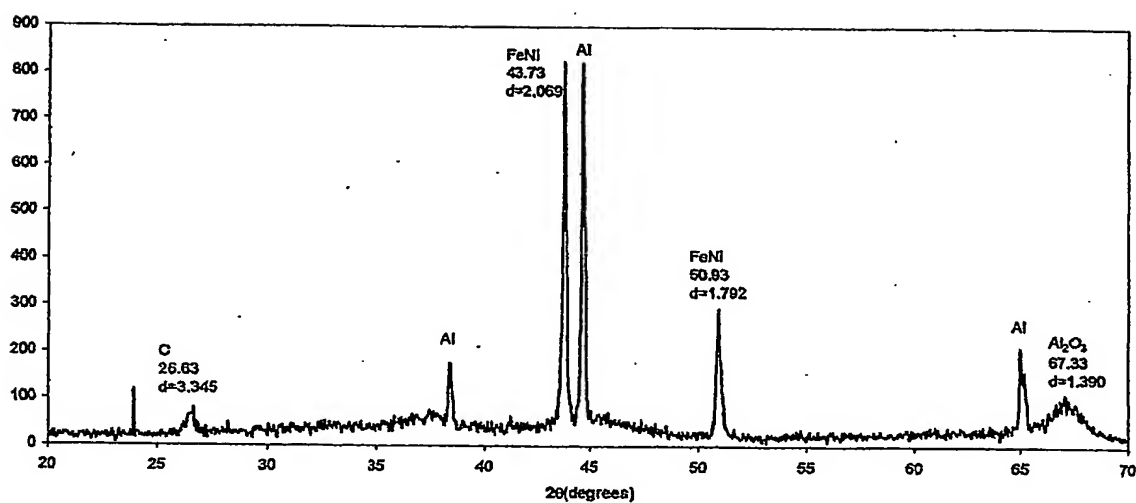


FIG. 2a

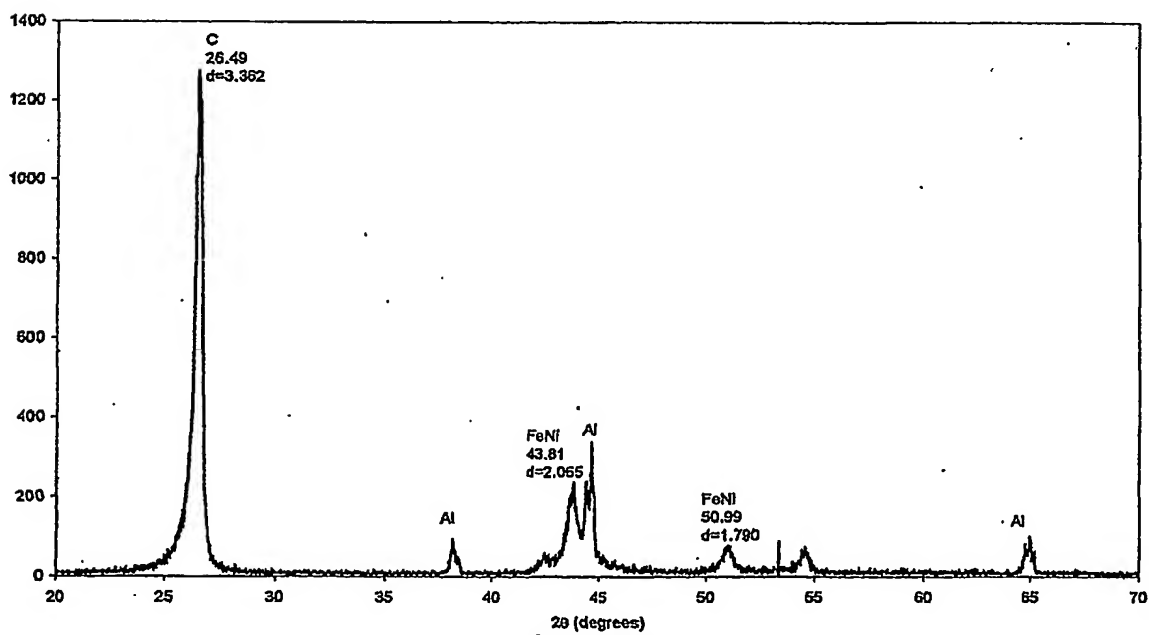


FIG. 2b

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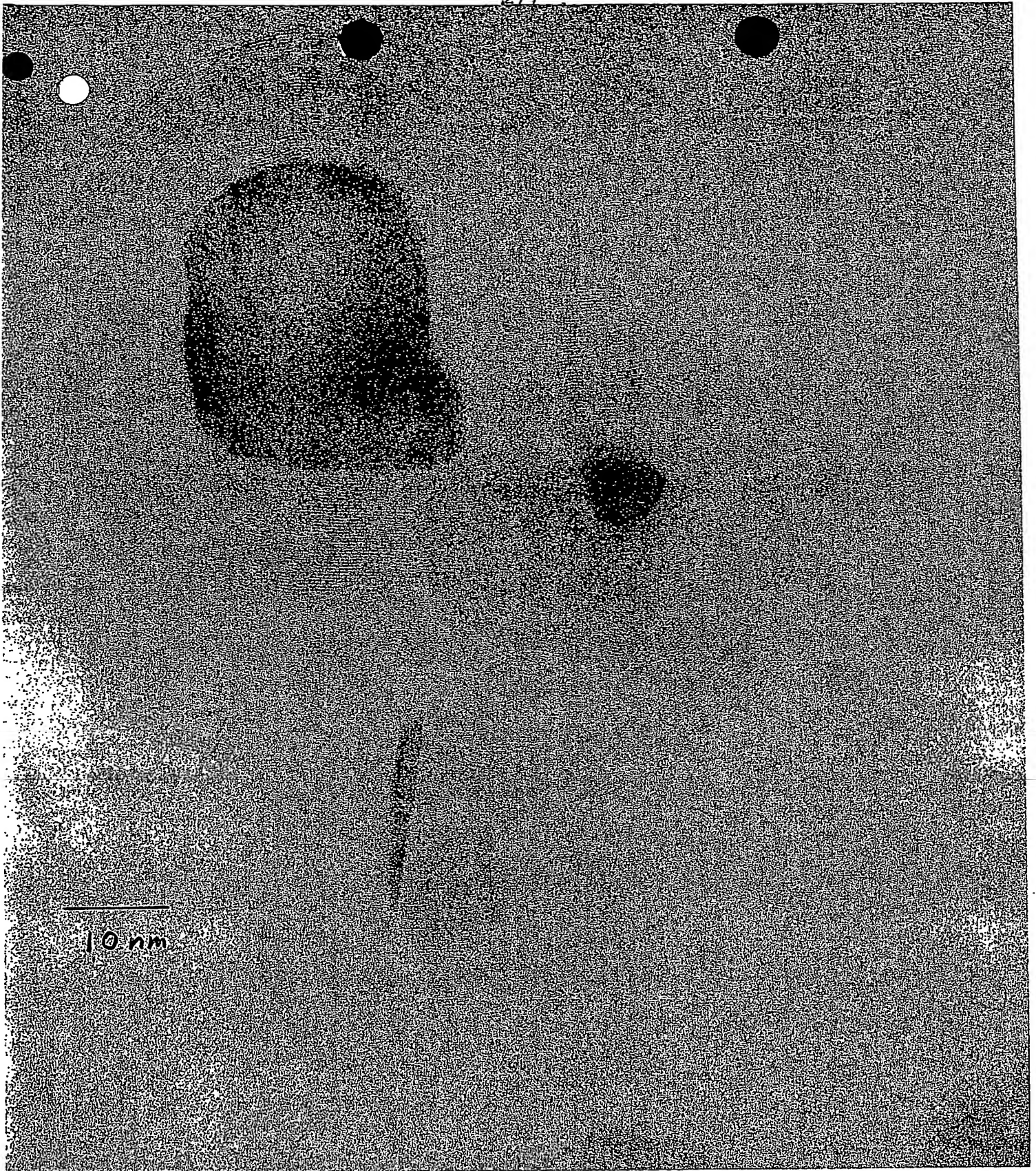


FIG. 3



FIG. 4

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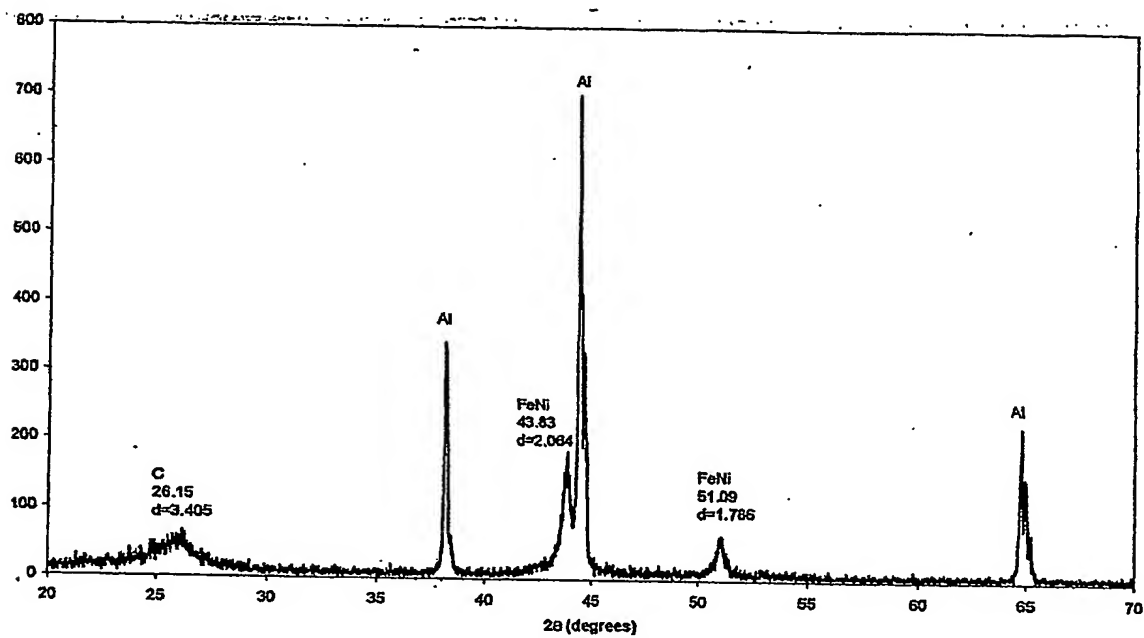


FIG. 5

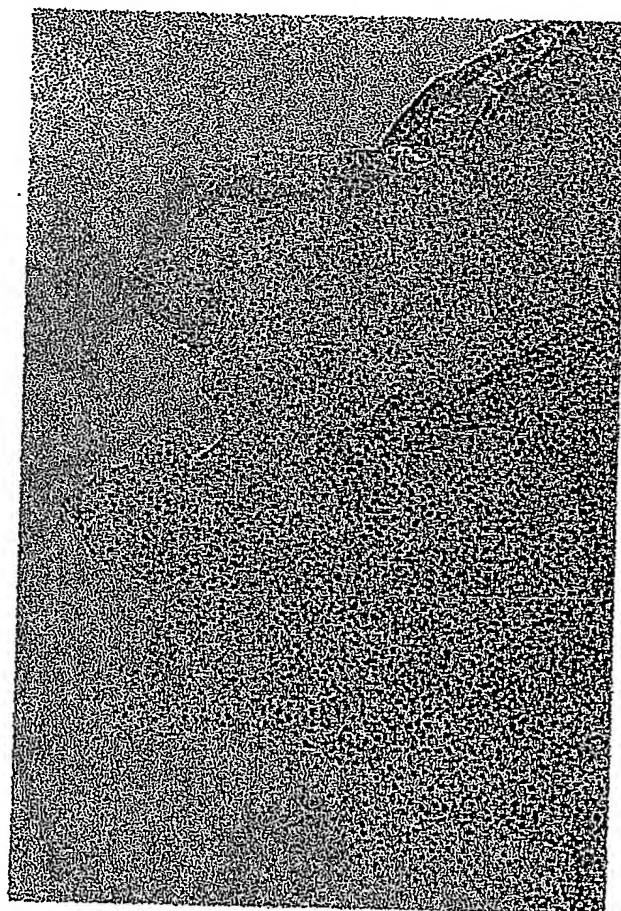


FIG. 6

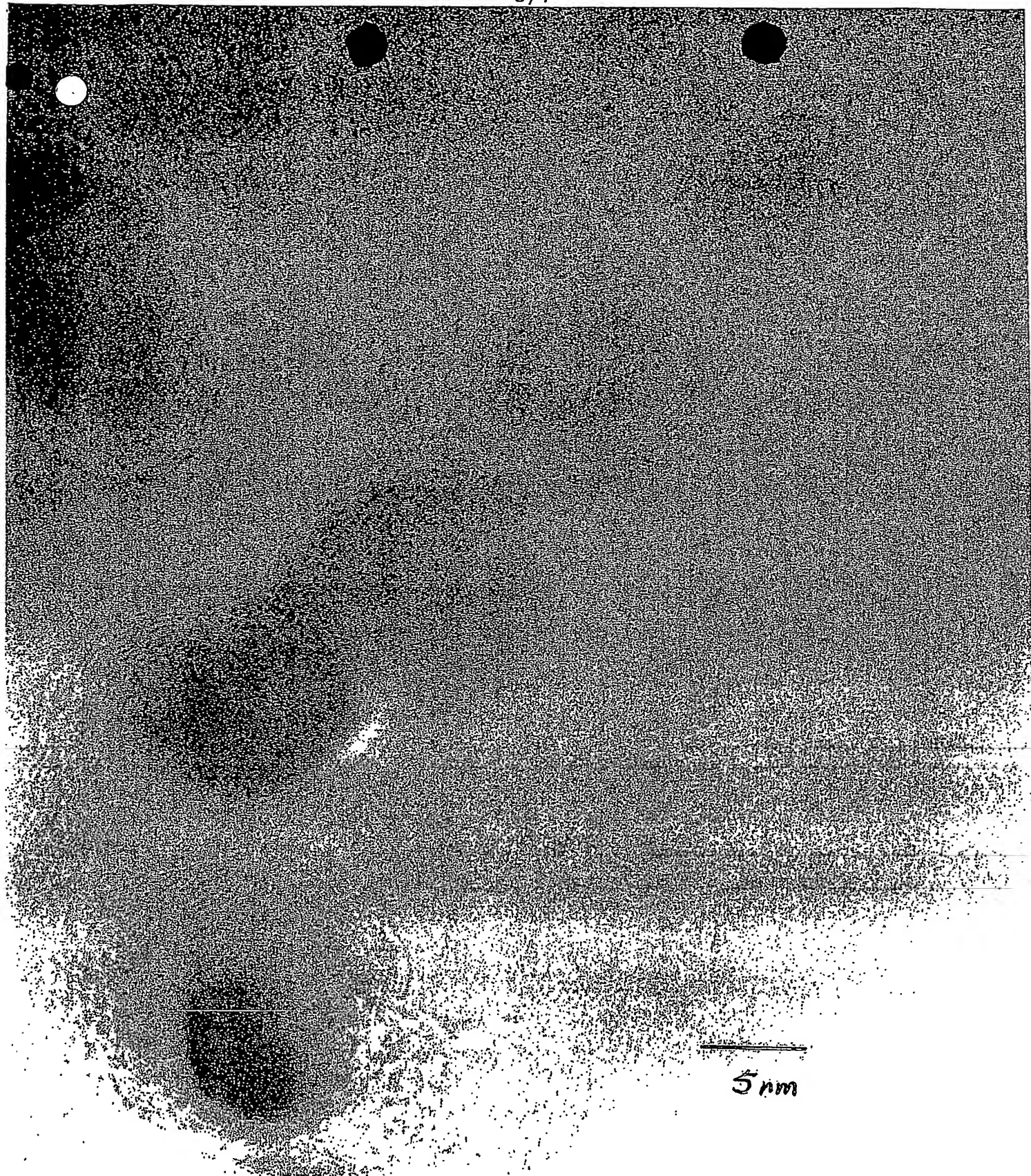


FIG. 7

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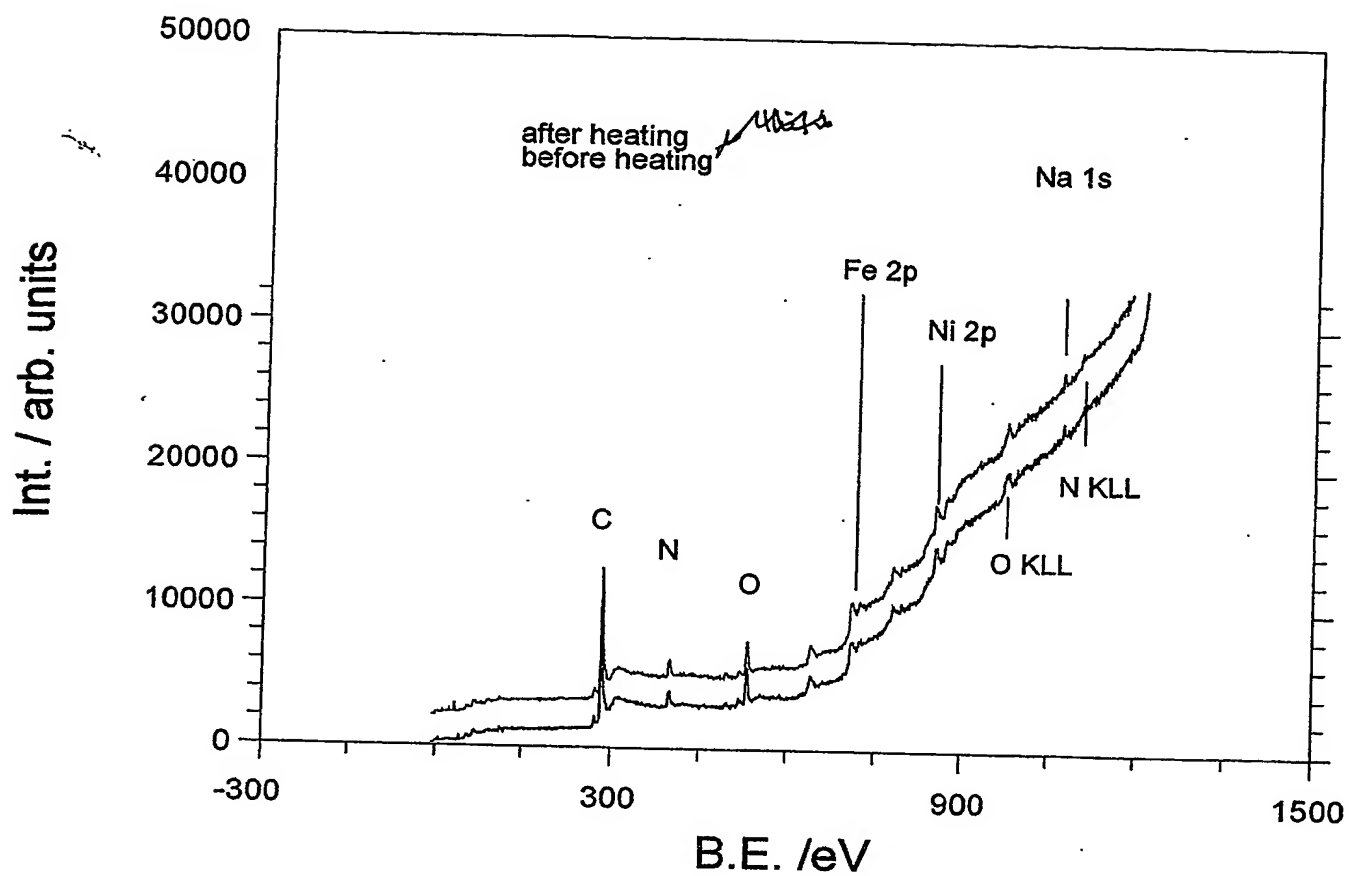


FIG. 8

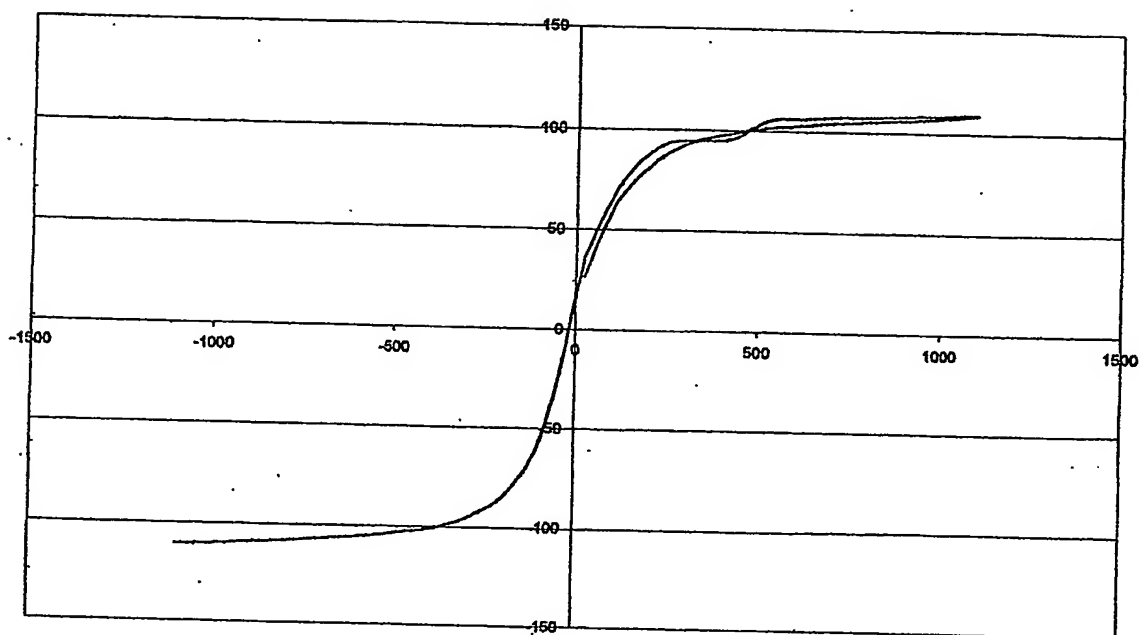


FIG. 9

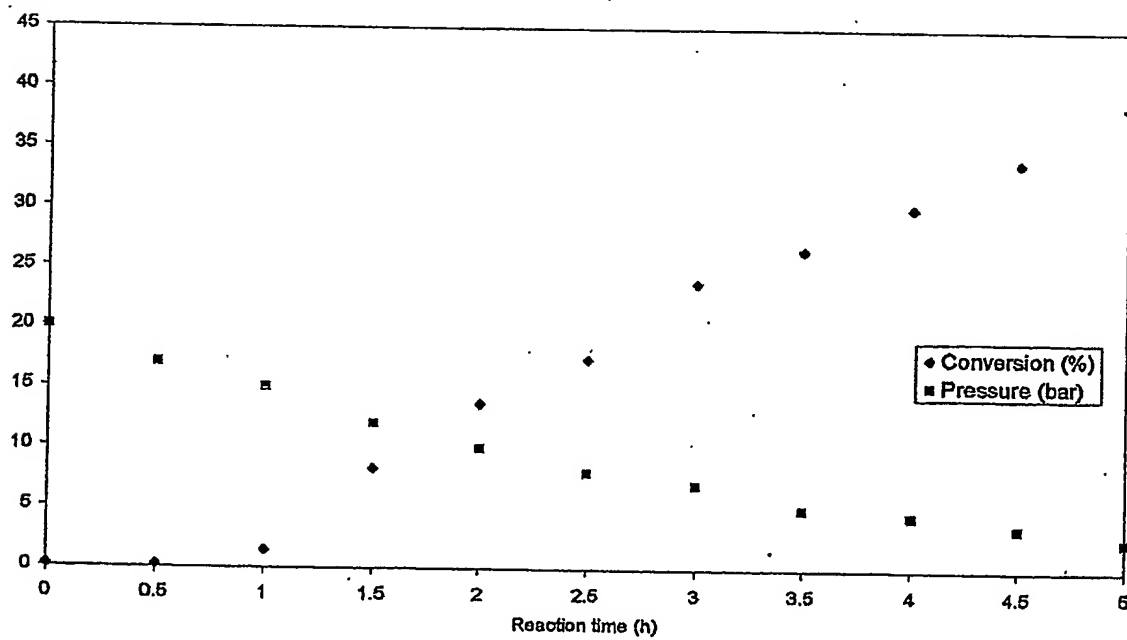


FIG. 10

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